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13. ABSTRACT (Maximum 200 words) Chromophores with improved molecular hyperpolarizability have been covalently incorporated into polymers which can be used to prepared optical quality spin cast thin films, poled near the glass transition temperature, and hardened to lock-in poling-induced electro-optic activity. A variety of lattice hardening protocols have been developed as used to prepare materials which show no significant loss of electro-optical activilty when examimed for 1000 hours at 100°C. Reactive ion etching is used to prepare buried channel waveguides and to integrate polymeric electro-optic modulator waveguide with silica fibers and VLSI semiconductor electronics. Materials have been provided to a number of companies and academic laboratories attempting to utilize polymeric electro-optic modulators.				
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DEVELOPMENT AND UTILIZATION OF DEVICE QUALITY NONLINEAR OPTICAL
MATERIALS

F49620-94-1-0312

Final Progress Report Submitted to

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REVIEW OF OBJECTIVES:

The primary objective of this contract is to develop processible nonlinear optical materials and processing protocols which permit fabrication of prototype electro-optic modulator devices and integrated opto-electronic circuits. This effort provides the primary materials support for device development efforts carried out by W. H. Steier at USC, H. Fetterman at UCLA, Y. Shi at TACAN, W. Bischel at Deacon Research, and R. Mustacich at RVM Scientific.

STATUS OF EFFORT:

An excellent overview of this effort is provided by the article "Polymeric electro-optic modulators" by L. R. Dalton published in Chemistry & Industry, No. 13, pp. 510-514, July 7, 1997 issue. A reprint of this article is provided as an appendix to this report.

Three classes of electric field poling/lattice hardening reactions have been developed for preparing thermally stable nonlinear optical materials exhibiting electro-optic coefficients in excess of 15 pm/V (Dalton, et al., Chemistry of Materials, 7, 1060-1081 (1995)). Thermally stability is defined as retention of 95% or greater of optical nonlinearity after 1000 hours at 100°C. Both intra and intermolecular condensation reactions have been used to lock-in poling-induced order and to harden materials sufficiently to permit subsequent processing. These efforts have permitted the fabrication of a variety of prototype electro-optic modulator devices and the performance of these devices has been demonstrated to 113 GHz (Chen, et al., Proc. SPIE, 3007, 314-317, 1997). Both reactive ion (reactive ion etching and electron cyclotron resonance etching) and photolithographic methods have been developed for preparing buried channel nonlinear optically active waveguides. These methods have been coupled with silicon v-groove techniques to develop mechanically stable coupling of polymeric waveguides with silica fiber transmission lines. Tapered transitions have been fabricated and tested to reduce optical loss due to mode size mismatch between silica fibers and polymer EO modulator waveguide. Recently processing protocols have been developed which permit integration of polymer electro-optic devices on non-planar silicon integrated circuits (e.g., VLSI wafers). Both vertical and horizontal integration has been demonstrated (Dalton, Chemistry & Industry, no. 14, 510-514, 1997).

Recently, London theory has been used to identify problems in poling efficiency and lattice hardening efficiency and show that these problems arise from chromophore-chromophore electrostatic interactions (Proc. Natl. Acad. Sci. USA, 94, 4842-4847, 1997). Problems of transient and non-transient chromophore association and aggregation can be circumvented by chromophore redesign. In particular, prolate ellipsoidal structures should be avoided in favor of spherical and oblate ellipsoidal structures. Pulsed poling protocols have been successfully used to overcome problems of chromophore association; such techniques exploit knowledge of orientation and distance dependence of electrostatic interactions which can be obtained from London theory calculations. Problems associated with electrical conductivity and photoconductivity effects have been identified and insight gained has been used to develop improved active polymer waveguides and improved cladding materials.

A detailed study of the effect of processing conditions upon modulator performance has been carried out. Optical loss due to material inhomogeneity associated with processing conditions has been investigated. Oligomer distributions and phase separation of crosslinking reagents in thermosetting reactions have been studied employing a variety of techniques including GPC. Not only have conditions

leading to reduced optical loss been defined but the reproducibility of production of acceptable modulators has been achieved. Poling-induced optical loss has also been systematically investigated. Such loss has been shown to arise either from surface damage due to corona poling or an electrophoretic effect involving high dipole moment chromophores. Again conditions have been defined which lead to lowest possible optical loss.

ACCOMPLISHMENTS/NEW FINDINGS:

Three different schemes have been devised for fabricating hardened polymeric NLO lattices. The first is a precursor route where a soluble and processible polymer containing an NLO chromophore is prepared and processed into optical quality films by spin casting. The material is then poled and a crosslinking reaction is initiated while the poling field is on. This lattice hardening reaction locks in the poling-induced noncentrosymmetric order (i.e., elevates the glass transition temperature of the polymer lattice). This process typically yields materials which retain optical nonlinearity (during dynamic assays) to temperatures greater than 170°C. The precursor route has the advantage of permitting use of solvents compatible with clean room operation and permits reproducible poling with minimal effort. An example of the precursor route is the LD-3 material (developed under this program) currently used by TACAN/Ipitek, AdTech, Radiant Research, Deacon Research/Gemfire and RVM Scientific. The second route involves the use of thermosetting materials such as in sol-gel processing. With this approach, poling and hardening processes are not well-separated and "stepped" poling protocols have been found to yield dramatically improved optical nonlinearities relative to single temperature/electric field poling. The thermosetting approach requires more effort to achieve optimal results but this approach does have the advantage of permitting high chromophore number densities to be obtained and is compatible with clean room processing. An example of this approach is the PU-DR19 material used by TACAN (Shi et al., IEEE J. Selected Topics in Quantum Electronics, 2, 289-99, 1996). The final approach started as a modification of polyimide chemistry where an intramolecular condensation (imidization) reaction is used to achieve lattice hardening. A variety of synthetic schemes were developed for incorporating chromophores into polyamic acid/polyimide polymers. This approach has the advantage of permitting excellent thermal stability of optical nonlinearity to be achieved but suffers from the requirement of harsh solvents which are difficult to use with clean room processing and which can effect chromophore stability when high $\mu\beta$ chromophores are used. These problems with the polyimide approach have been addressed recently by generalizing the synthesis of heteroaromatic polymers exploiting both intra and intermolecular condensation for lattice hardening. This generalization permits precursor polymers with improved solubility in conventional processing solvents to be prepared.

With all of the above approaches, attention must be given to chromophore aggregation associated with strong electrostatic interactions. Such interactions can be overcome by improved chromophore design and by utilization of pulsed poling protocols.

New processing techniques, e.g., laser-assisted poling and molecular self-assembly assisted poling, have been developed to improve the order parameter for noncentrosymmetric alignment of chromophores in polymeric materials. Laser-assisted poling is particularly important for development of devices (such as 100 GHz modulators) employing in-plane electrode configurations.

Major progress has been made in the area of fabrication of buried channel nonlinear optical waveguides and in the interface (coupling) of such polymeric waveguides to silica fiber optic transmission lines. The Dalton and Steier groups at USC have pioneered the use of reactive ion etching techniques and new photolithographic techniques for the fabrication of buried channel waveguides characterized by reduced optical loss. Electron cyclotron resonance etching, which facilitates greater control over plasma conditions, has been shown to permit realization of smoother channel walls (hence reduced optical loss) than can be achieved by conventional reactive ion etching. Reactive ion processing has been used to effect silicon v-groove etching which, in turn, has served as the basis for precise alignment of polymer and silica waveguides and the development of mechanically-stable, low loss couplings.

Optical loss due to mode mismatch has been dramatically reduced by fabrication of tapered transitions (A. Chen et al., Proc. SPIE, 3005, 65-76, 1997). Such tapered transitions have been generated both by reactive ion etching (RIE) and multicolor photolithography (MCP) processing methods.

The final area where major progress has been made is that of integration of polymeric optical circuitry with semiconductor electronic circuitry. We have demonstrated that an NLO active polymeric waveguide structure can be fabricated on a planarized VLSI semiconductor wafer and that integration can be accomplished without degradation of either electronic or optical circuit function.

The above advances in processing and materials technology has permitted demonstration of electro-optic modulation to 113 GHz and has permitted the first demonstration of integration of polymeric and semiconductor circuitry. The materials effort supported by this contract has permitted fundamental questions to be answered concerning the feasibility of utilizing polymeric materials for commercial modulator applications.

As noted in the Chemistry & Industry article, work under this contract has achieved for the first time polymeric electro-optic modulator materials which are competitive and even superior to lithium niobate in terms of electro-optic coefficient, permit greater bandwidth to be achieved, permit easy integration with semiconductor electronics and silica fiber optics, and exhibit excellent stability in field tests. Further material improvements (particularly further improvement in electro-optic coefficient and reduction in optical loss at various operating wavelengths) are necessary for wide scale commercial application; however, work performed under this contract has set the stage for initial niche commercial applications.

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Fritz Strohkendl, Postdoctoral Fellow, partial support
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INTERACTIONS/TRANSITIONS:

INVITED LECTURES:

1. Third International Conference on Frontiers of Polymers and Advanced Materials, Kuala Lumpur
2. 28th Organosilicon Symposium, Gainesville, Florida
3. 1995 ACS/PMSE Symposium on Polymeric Organic Materials: Solid State Properties and Smart Materials, Anaheim, California
4. Materials Research Society Symposium on Thin Films for Integrated Optics Applications, San Francisco, California
5. National Technology Transfer Center, Technology Applications Review, Orlando, Florida
6. NASA Lecturer, Fifty Fourth Frontiers in Chemistry Lecture Series, Cleveland, Ohio

7. NATO Advanced Research Workshop on Photoactive Organic Materials: Science and Applications, Avignon, France
8. SPIE International Symposium on Nonlinear Optical Properties of Organic Materials VIII, San Diego, California
9. SPIE International Symposium of Optical and Photonic Applications of Electroactive and Conducting Polymers, San Diego, California
10. SPIE International Symposium on Fullerenes and Photonics II, San Diego, California
11. Symposium on Optoelectronic Materials and Conjugated Polymers, IV International Conference on Advanced Materials, Cancun, Mexico
12. 7th International Conference on Unconventional Photoactive Systems, Stanford, California
13. OSA/ACS Organic Thin Films for Photonics Applications, Portland, Oregon
14. International Business Communications Conference on Commercial Applications for Organo Electronic Materials, Marina del Rey, CA
15. Society of Plastics Engineers (SPE) annual technical meeting ANTEC, Indianapolis, IN
16. American Chemical Society National Meeting, New Orleans, LA
17. American Chemical Society National Meeting, Orlando, FL
18. SPIE International Symposium on Fullerenes and Photonics III, Denver, CO.
19. ACS/OSA Symposium on Organic Thin Films for Photonic Applications, Orlando, Florida
20. International Conference on Nonlinear Optics 3, Marco Island, Florida
21. Fourth International Conference on Frontiers of Polymers and Advanced Materials, Cairo, Egypt
22. Symposium on Dendrimers and Hyperbranched Polymers, Spring American Physical Society National Meeting, Kansas City, Mo.
23. National Meeting, ANTEC, Society of Plastics Engineers, Toronto, Canada
24. AFOSR/ONR Photonic and Electro-Optic Polymer Review, Atlantic Beach, Florida
25. Sino-American Topical Meeting and Exhibit, Solid State Lasers: Materials and Applications, Tianjin, People's Republic of China
26. Gordon Conference on Organic Thin Films, Salve Regina
27. The International Society of Optical Engineering 42nd Annual Meeting, San Diego, CA.

INVITED SEMINARS:

Numerous seminars at various industries, government laboratories, and universities including seminars at University of Florida, University of Illinois, University of Washington, NASA Marshall Space Flight Center, University of California at Los Angeles, the Max-Planck-Institut fur Polymerforschung (Mainz FRG) and the Optical Science Center of the University of Arizona.

Presentations were also made before the Board of Gemfire Corporation, senior management of Hughes Research Laboratories, the Board of the Loker Hydrocarbon Research Institute and the Board of Trustees of the University of Southern California, etc.

CONSULTATIVE AND ADVISORY PANEL SERVICE:

1. Blue Ribbon (Final Phase) Panel for the Selection of Presidential Faculty Fellows (National Science Foundation)
2. Consultant, Medical Research Service, Veterans Administration
3. Materials Research Science & Engineering Center Panel, National Science Foundation
4. Panel 15, Office of Energy Efficiency and Renewable Energy Photovoltaics Review, U.S. Department of Energy
5. Advisory Committee, National Institutes of Health Biomedical Technology Centers at the University of Illinois and at Dartmouth University
6. Consultant, Arizona Disease Control Research Commission, State of Arizona
7. Immunobiology Study Section, National Institutes of Health
8. Advisory Committee, The New York Herman F. Mark Institute for Polymers Science and Engineering at the Polytechnic University, NY, NY
9. Editorial Advisory Board, Chemistry of Materials, American Chemical Society
10. Consultant, Princeton Materials Research Center.

INTERACTIONS AND TRANSITIONS:

Research Interactions and Technology Transitions include EniChem/ROI Tech/Lightwave Microsystems Corp. (A. Jen/J. Kenney), Cal Tech/JPL (S. Marder and J. Perry), Hughes Research Laboratory (U. Efron), TACAN/Integrated Photonics Technology, Ipittek (Y. Shi), AdTech (S. Sinha), Deacon Research/Gemfire (W. Bischel), RVM Scientific (R. Mustacich), IBM (D. Burland), Physical Optics Corporation (G. Savant), and Thermax Systems, Inc. (Bruce Sangster), Radiant Research, Inc (B. Davies and R. Chen). Also interacted with the Los Angeles Regional Development Association (LARDA).

NLO active polymeric films were provided to TACAN/Ipittek, RVM Scientific, Deacon Research/Gemfire and Physical Optics Corporation to permit these organizations to pursue evaluation of these materials for prototype device development. TACAN and POC are interested in low frequency, low cost modulator fabrication. TACAN is interested in evaluating the long term, in-field performance of polymeric electro-optic modulators. RVM Scientific is interested in using new photolithographic techniques to fabricate low loss waveguides and low loss transitions from polymer waveguides to silica fiber transmission lines. Deacon Research is interested in fabricating full color, flat panel displays from polymeric electro-optic modulators.

Photoactive chromophores were transitioned to Hughes Research Laboratory for use in development of high density optical memories.

Thermax Systems, Inc. Is interested in using photoactive chromophores in cooling applications.

Discussions have been held with Exxon, Allied Signal and Audemars Corporations and with NASA Marshall Space Flight Center who have expressed interest in collaborating and participating in technology transfer.

INVENTIONS:

None

HONORS/AWARDS

1. The 1996 Richard C. Tolman of the American Chemical Society (April 23,1997)

2. Paul C. Cross Endowed Lectureship in Chemistry, University of Washington, Seattle, WA, May 29, 1996
3. NASA Lecturer, 54th Frontiers of Chemistry Lecture Series, Case Western Reserve University, Cleveland, OH, April 27, 1995.
4. Harold and Lillian Moulton Distinguished Professorship of Chemistry (Endowed Chair), University of Southern California
5. Scientific Co-Director of the Loker Hydrocarbon Research Institute, University of Southern California
6. Nominated for the National Academy of Science
7. Nominated for the Chemistry of Materials Award of the American Chemical Society

The research has been featured in the news articles in the following publications: The Baltimore Sun newspaper, Chemical & Engineering News, Research & Development Magazine, Laser World Focus, Business Week, Science, BMDO Update, Wired Magazine, Photonics Spectra, Chemistry & Industry, Polymer Science News, Photonics Science News, Ind. Eng. Chem. Res., etc. A television episode of "Strange Universe" will focus on the research; the filming was completed recently at the Loker Hydrocarbon Research Institute. The research has been featured on two occasions on local radio broadcasts.

Note: Mr. Aaron Harper, who worked on this project both as a graduate student and briefly as a postdoctoral fellow, was the first recipient of the American Chemical Society Organic Division Fellowship. This fellowship provided partial salary support for Mr. Harper. Mr. Harper is now an Assistant Professor of Chemistry at Texas A&M University.

ASSERT Evaluation Report

F49620-95-1-0450, An ASSERT Proposal for the Development of Advanced Polymeric E-O Modulators

During the support-period to 9/1/97, Theresa Axenson received support to carry out materials synthesis and processing activities relevant to the fabrication of advanced electro-optic modulators. This research resulted in several significant improvements in polymeric electro-optic modulator technology. The evaluation of modulators fabricated employing new technology has been extended to 113 GHz and recently vertical integration of the modulator with VLSI electronics has been demonstrated (see article by L. Dalton, Chemistry & Industry, no. 13, 510-514, 1997). Training of Ms. Axenson involved laboratory research (including training in state-of-the-art synthetic methods and use of analytical instrumentation), group meetings and symposia involving graduate and undergraduate students pursuing research under the direction of Dr. Dalton, joint research group meetings involving the research groups of Professor William Steier (USC Electrical Engineering), Professor Robert Hellwarth (USC Electrical Engineering/Electrophysics), Professor Harold Fetterman (UCLA Electrical Engineering) and Professor Dalton and meetings with visiting scientists from industrial laboratories (participating in BMDO or AFOSR research programs). Visiting industrial scientists (receiving BMDO support) included Dr. William Bischel (Deacon Research) and Dr. Robert Mustacich (RVM Scientific). During this period, a constant interaction was maintained with Dr. Y. Shi of TACAN Corporation. As Ms. Axenson has completed all formal course requirements for the Ph.D. and has passed her Ph.D. qualifying examination, she did not take formal courses but did benefit from a rich seminar program including by such distinguished visitors as Dr. F. Kajzar (CEA, France), Dr. Joseph Zyss (France Telecom), Dr. John Reynolds (Univ. of Florida), and Dr. Robert Grubbs (Cal. Tech.). Ms. Axenson's research involved the first effort to incorporate high $\mu\beta$ chromophores into polymer lattices. Three different schemes were developed for stabilization of poling-induced noncentrosymmetric chromophore order. The first is a precursor polymer route where a soluble and processable polymer, containing an NLO chromophore as a pendant to the polymer main chain, is prepared and processed into optical quality films by spin casting. The material is then poled and a crosslinking reaction is initiated while the poling field is on. This lattice hardening reaction locks in the poling-induced noncentrosymmetric order (i.e., elevates the glass transition temperature of the polymer lattice). The process typically yields materials which retain optical nonlinearity to temperatures as high as 170°C (during dynamic assays). The precursor route has the advantage of permitting use of solvents compatible with clean room operation and permits reproducible poling with minimal effort. The second route involves use of thermosetting materials such as in sol-gel processing. With this approach, poling and hardening processes are not well-separated and "stepped" poling protocols have been found to yield dramatically improved optical nonlinearities relative to single temperature/electric field poling. The thermosetting approach requires more effort to achieve optimal results but this approach does have the advantage of permitting high chromophore number densities

to be realized. The final approach utilizes intramolecular crosslinking (as in the imidization reaction) to achieve lattice hardening.

Ms. Axenson also worked on extension of London theory to provide the first quantitative understanding of the role of chromophore electrostatic interactions in defining poling efficiency and lattice hardening efficiency observed for high dipole moment/high polarizability chromophores. She also pioneered the development of new spectroscopic techniques for characterizing both optical nonlinearity and photochemical stability. Her work during the past year has already resulted in several publications (with more to follow from work already completed) and has resulted in several invited lecture presentations including an SPIE presentation and a presentation at the Naval Research Laboratories in Washington.